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(71) Applicant *(for all designated States except US)*: TECHNION RESEARCH & DEVELOPMENT FOUNDATION LTD. [IL/IL]; Technion City, 32000 Haifa (IL).

(72) Inventors; and
(75) Inventors/Applicants *(for US only)*: REIN, Dimitry [IL/IL]; Apartment 13, 4 Lilach Street, 36821 Nesher (IL). VAYKHANSKY, Lev [IL/IL]; Apartment 11, 1 Habas Street, 33393 Haifa (IL).

(74) Agent: LAVIE, Simon; P.O. Box 6202, 31060 Haifa (IL).

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(57) Abstract

The present invention relates to a polyolefin composite material based on fiber and a matrix of a polyolefin, selected from polyethylene and polypropylene possessing improved mechanical properties. The polyolefin composite comprises a network of fibers and matrix which have a molecular weight of above 500,000. This network is held together by compressed and crystallized molecular brush layers, obtained by the swelling of the external surface of said fibers and reciprocal entanglement with it of the polymer matrix. The composite material provides a tensile strength of at least 75 % of the volume average tenacity of the polyolefin fiber network and matrix. A process for obtaining a polyolefin composite material and the improved properties of the resulted product are also described.

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COMPOSITE MATERIALS BASED ON ULTRA-HIGH MOLECULAR WEIGHT POLYOLEFIN FIBER AND MATRIX, AND PROCESS FOR THE MANUFACTURE THEREOF

The present invention relates to novel polyolefin composites. More particularly, the invention relates to novel polyolefin composites material based on fiber and matrix of ultra-high molecular weight of polyolefin and to a process for the manufacture thereof.

BACKGROUND OF THE INVENTION.

Polyolefins are considered non-polar polymers, used for many purposes such as, filaments, tapes, fibers, films, etc. One of the main field of polyolefins use is in the manufacturing of composite materials.

As known, a main problem encountered with production of composites, is the non-polarity of the polyolefins, which causes difficulties in obtaining a good adhesion between the non-polar polyolefins and the extraneous materials, such as plastic or resin, which generally are more polar than the polyolefins.

Ultra-high molecular weight polyethylene (hereinafter referred to UHMWPE) is a linear high density polyethylene (HDPE) with a molecular mass in the range of between 1 X 10^6 to 16 X 10^6. Its very high molecular mass imparts an exceptional impact strength and abrasion resistance as well as special processing characteristics. These unusal properties preclude the use of conventional extrusion and moulding techniques.

Fibers made from this type of polyethylene are characterized by their high modulus and strength, light weight and high energy dissipation in comparison with other polymer fibers. However, the standard extrusion and molding techniques for obtaining fibers of UHMWPE are not applicable.

A main deficiency of UHMWPE fibers in its use as reinforcement in composites materials, is their relatively poor adhesion to the matrix in a composite and their chemical inertness as mentioned in a recent review (D.N. Hild et al, J.Adhesion Sci. Technol. 6,p.879, 1992). As known, the stress-transfer ability of the fiber-matrix interface and accordingly the mechanical properties of such composites are greatly affected by the level of the fiber-matrix adhesion. The compatibilty between the thermoplastic UHMWPE fibers and the thermoset resins is also limited due to the non-polar property of the polyethylene.

Composites of polyethylene and UHMWPE, obtained by hot compression molding at a temperature between the melting points of the fibers and the polyethylene matrix, were found to comprise a uniform transcrystalline layer of the polyethylene melt on the UHMWPE fiber surface (Teishev et al. J.Appl.Polym.Sci., 50, 1993, p.503).

The European Patent Application Number 313,915 is suggesting a process to improve the adhesion of polyolefin objects to polar polymer matrices. The process involves a treatement of the surface of polyolefin objects obtained from a solution or melt, having a molecular weight of at least 400,000 g/mol, by its immersion into a solvent at a temperature above that of the polyolefin dissolution. A most preferred solvent which is suggested is xylene. It is claimed that the treated objects according to this process retain their adhesive strength to the polar matrices for a long period of time.

In the U.S. Patent Number 4,563,392, it is described a method for obtaining a coated polyolefin fiber having an increased adhesion to matrix materials. According to this method the multifilament fiber having a molecular weight of above 500,000, is coated with a polymer possessing the

ethylene or propylene crystallinity, said coating being between 0.1% to about 200% by weight of the fiber.

According to a very recent paper by Roger S. Porter et al (Polymer, 35, 23, 1994, p.4979-84),high-modulus and high-strength UHMWPE bars or films are obtained, by a two-stage drawing technique: by direct compaction followed by calendering at a temperature below the melting point.

In another recent paper by B.L.Lee et.al. (Journal of Composite Materials, Vol. 28, No.13.1994, p.1202-26), there are described tests which were carried out on polyethylene fiber-reinforced composites and examined under ballistic impact loading.

The above brief review, illustrates that the subject of fiber and matrix of UHMWPE composite material is indeed considered an interesting problem which indicates that it requires more investigation.

It is an object of the present invention to provide novel composite materials based on fiber and matrix of UHMWPE.

It is another object of the present invention to provide a process for obtaining composite materials based on UHMWPE having improved mechanical properties. It is yet another object of the present invention to provide a process for obtaining a material based on fibers of UHMWPE with improved adhesion property to a polymer matrix.

BRIEF DESCRIPTION OF THE INVENTION.

The invention relates to a polyolefin composite material based on fiber and matrix (hereafter referred to composite material) of a polyolefin selected from polyethylene and polypropylene possessing improved mechanical properties, comprising a net-work of fibers and matrix having a molecular weight of above 500,000, said net-work being

held together by compressed and crystallized molecular brush layers obtained by swelling of the external surface of said fibers and reciprocal entanglement with it of the polymer matrix. According to a preferred embodiment, the tensile strength of said composite material is at least 75% of the volume average tenacity of the polyolefin fiber net work and matrix. A process for obtaining the polyolefin composite material as well as the significant advantages thereof are also described.

DESCRIPTION OF THE FIGURES.

Figure 1, shows a SEM micrograph of a model sample of a composite prepared on a glass plate. The fiber under observation being near the glass surface. As can be noticed, the growth of UHMWPE fiber surface, i.e. crystallized brush layers, entangled with the fiber surface molecules before compression. It appears that the lamellae are perpendicular to the fiber surface.

Figure 2, illustrates in a graphic manner the transversal stress-percentage elongation of said composite material at a temperature of 25°C. This graph illustrates the much higher elongation property compared with typical composites (about 1%).

Figure 3, shows the X-ray diffraction pattern of the unidirectional composite material obtained in Example 4, after an ultimate transversal elongation at 25°C (at fiber axis - vertical).

As can be noticed, from Figure 3, the reflex (a) on the pattern, is caused by the oriented crystalline matrix. This feature is unique for all types of composites which

are subjected to transversal elongation. It also proofs the extremely high adhesion which exists between the fibers and matrix inher nt to the obtained composite material and to the unusual properties of UHMWPE matrix obtained from the solution.

DETAILED DESCRIPTION OF THE INVENTION.

According to the present invention,the composite material consists of unidirectional fibers,yarns,layers or cloths. Before and after the elongation process in a direction transverse to the fibers, there are two different materials, which can be used for different purposes. Before the elongation, the composite is a non-isotropic material which possesses a relatively low matrix modulus and strength which is most useful, e.g for ballistic protection. After elongation of at least 300% and even more, the composite material will possess a high modulus, a high strength and a low creep of below 1.5% and even close to the melting point, in any desired directions; such composites are particularly useful as construction materials.

It was found that the entangled molecular brush layers, present in the polyolefin composite materials are obtained by the swelling of the fiber-based external surface, under conditions prevailing in the process as described in the present invention, and the reciprocal entanglement with it of the polymer in solution.

As known, swelling is a chemical property related to an interaction between a polymer and a solvent, which can be described as a penetration of the solvent molecules into the inter-molecular space of the polymer, weakening by them of the intermolecular int ractions and

alienation of the polymer molecules into said solvent. It is the reversible dimensional changes that occur when fibers undergo an absorption process. Since fibers are structurally anisotropic, they undergo greater transverse versus longitudinal swelling.

No particular information is mentioned in the literature relating to the kinetics of a simultaneous swelling and dissolution in polymers.

According to the present invention, the matrix of the ultra-high molecular weight polyethylene, is obtained as a result of the property of the respective solution to produce, under the prevailed conditions, "gel-like sperulites" due to the inclusion of a large amount of solvent of up to 90%. Most preferred solvents used for said polyethylene are selected from xylene, decalin, tetralin and paraffin oil or any mixture thereof. Upon applying even a low pressure of about 50 atmospheres, a multilayer lamellar structure is formed, being oriented parallel to the plane of compression.

The polyethylene constituent to be used as matrix should possess an average molecular weight of at least 500,000 and preferably above 3,000,000 and most preferably in the range of 5,000,000 to 8,000,000, being substantially equal to the molecular weight of the fibers material.

Composite compaction has to be carried out under heating at a temperature, which is above the melting temperature of the polyolefin matrix but below the melting point of the loaded polyolefin material. The compression, may be carried out in a broad range of between 0.05 to 300 MPa for a period of between 5 minutes to 25 hours.

It was found that the composite material consisting of UHMWPE fibers according to the present invention has the following properties:

- a low density of 0.98 g/cm^3, i.e. lighter than water;
- a high tranversal strength of composite material i.e. at least 25 MPa for a 30% matrix composite;
- a high shear strength of at least 25MPa;
- a high elongation in direction transverse to fiber axis of at least 70% at 25°C;
- a high ultrasonic tensile modulus of at least 120 GPa for a 30% matrix composite;
- a high tensile strength of at least 1.5 GPa for a 30% matrix composite;
- high properties at the cryogenic temperature; thus at a temperature down to that of liquid helium UHMWPE based composites have the lowest dielectric and loss characteristics for radar operating frequencies within the millimetric frequency range; thus at frequencies up to 54 GHZ, the dielectric constant remains invariable at 2.25 and loss tanget at 0.0006;
- an outstanding aptness for sonar technology, i.e. sonar domes; thus in UHMWPE composites reflection of the sound waves at all angles of incidence is minimal because the sound speed and the density of the composite and sea-water are closely matched;

In view of the above properties, the material can be easily work up by ordinary machining without any crack formation. Among the various uses as a construction material, the following may be mentioned: aircraft and spacecraft parts, helicopter structures, sonar domes, radoms, marine applications in deep underwater, surface effect ship and hydrofoil craft, antennas, sport goods, high pressure tanks, neutron and radiation shields, structural elements at cryogenic temperature, military applications, prosthesis, battery separators, microporous ultra-strength membranes for water and industrial sewage

purifying, as additives in flame retardant material, etc. The invention also provides a method for the preparation of the composite material based on fiber and matrix of UHMWPE. The method comprises the following steps:

(a) Swelling of the UHMWPE fibers, whereby the solvent molecules penetrate into the inter-molecular space of the polymer. The swollen surface layer, serves as a disentanglement zone and thus become more free. The dissolution of the polyolefin objects in the solvent, or solution of the matrix forming polymer, at temperatures above that of the matrix bulk polyethylene, can be retarded by a preliminary loading of the respective polyolefin objects;

(b) growing of the "brush" layers from dissolved UHMWPE molecules entangled with the swelled UHMWPE fiber surface;

(c) growing supermolecular structures, i.e. crystallization of the brush layers, entangled with the fiber surface molecules and with the polymer molecules in the solution which accompanies them;

(d) compressing or molding the super molecular structures accumulated on the fiber surface, whereby a semi-product coating of the composite material is obtained; according to a preferred embodiment, this compression is carried out on fibers covered by gel-like spherulites, thus obtaining on the fiber surface a well packed zone having a high degree of regularity cover, and

(e) molding under heating and compression the semi-product coating, whereby the desired modifications and properties are imparted to the composite

material.

The temperature which should prevail during the swelling, (step a), should be above the dissolution point of the polyolefin objects without loading, generally being below its melting point under the current conditions.

The tension applied in the first step (a) should be applied preferably by a force of between 0.1% to 30% of the force at break of the respective material.

The solvent used for obtaining the solution of the polyolefin matrix, may be selected from a broad class of solvents, provided that it possesses an interaction parameter (x) with the dissolved polymer in the range of between 0 to 0.3, at the treatment temperature in steps (a) and (b).Typical examples of such solvents are:xylene, tetralin, decalin, parafin oil, or mixtures thereof.

The preferred concentration of the polyethylene solution is between 0.1% to 10% by weight and most preferred between 1% to 3% by weight.

The temperature which prevails during the crystallization in step (c) is generally between 20° to 120°C.

The composite materials obtained according to the present invention possess a number of improved characteristics in respect to good mechanical and ballistic properties, such as: improved tensile strength and elastic modulus at least 1.5 GpA and 120 GPa, respectively, a high energy absorption, a interlaminar shear strength of at least 25 mega-Pascal and a transversal strength of at least 25 mega-Pascal. As a result of the above properties, they will have a wide range of technical applications, such as: in boats manufacture, in aircraft parts, in printed circuit boards, ballistic protection armours, car parts, radomes, prosthesis etc.

The invention will be hereafter illustrated by the following Examples, being understood that these Examples are presented only for a better understanding of the invention, without imposing any limitation thereof. A person skilled in the art will be in a position, after reading the present specification, to insert slight modifications without being outside the invention as covered by the attached Claims.

EXAMPLE 1.

A matrix was prepared from a solution of 1.5% by weight of polyethylene having an average molecular weight of about 3,000,000 in tetraline. The commercial yarn of UHMWPE (Trade Mark Spectra1000) having a tensile strength of 33 g/den and modulus of 1800 g/den, was chosen for the respective tests.

Value of load for monofilament was about 2 g, temperature of treatment of about 130°C and time of treatment of about 5 minutes.

An amount of matrix from a solution (mats) was compressed with the monofilament in a cylinder of 2 mm diameter at a pressure of 20 MPa. The results of pull-out tests which were carried out were as follows (the data are given in MPa):

Table of pull-out tests.

Fibers	Composite matrix consists of dried mats	coagulated in alcohol mats	wet with tetralin mats.
Untreated	0.6-1.7		1.5-3.5
Treated in pure tetralin without drying	1.3-2.2		3.0 - 3.5
Treated in solution, crystallization and drying by vacuum	1.7-4.0		4.0 - 6.5
Treated in solution crystallization and coagulation in alcohol without drying			7.0-9.0
Treated in solution crystallization and maintained wet with tetralin	9.0-12		12-16

EXAMPLE 2.

A yarn of ultra-high molecular weight of a commercial fiber polyethylene (Trade Mark Spectra 1000) having a tensile strength of 33 g/den and modulus of 1800 g/den, was tensile loaded by a force of 0.3 kg. The resulted loaded yarn was treated for six minutes with a solution of 1.5% by weight of polyethylene having an average mole-

cular weight of 3,000,000 in tetralin at a temperature of 135°C.

The treated yarn was quenched in the same solution for 10 minutes at a temperature of 110°C. The resulted polyethylene yarn, was dried by vacuum, obtaining a yarn pre-preg material consisting of a 10% by weight of the matrix material.

EXAMPLE 3.

A solution of 1.5% by weight of polyethylene having a molecular weight of 3,000,000 was prepared and then cooled and filtered through a glass filter. The resulted sedimented polymer on the filter was compressed at 5MPa, producing a polyethylene plate.

The yarn pre-preg obtained in Example 2, was winded on a steel plate thus producing unidirectional layers. The polyethylene plates were put between two unidirectional layers, producing a "sandwich" material, which was compressed at 10 MPa, obtaining unidirectional pre-preg having about 40% matrix material content.

EXAMPLE 4.

The yarn as in Example 2 was tensile loaded by a force of 0.4 kg. The resulted loaded yarn was treated at a temperature of 130°C with a solution of tetralin containing 1.75% of polyethylene having an average molecular weight of 3,000,000, for about 8 minutes. The treated yarn was cooled slowly to room temperature for about 20 minutes, while the temperature of the surrounding solution was maintained unchanged.

The yarn pre-preg obtained was winded on a steel plate, thus producing uni-directional layers and compressed at

15 MPa for about 30 minutes, the temperature being gradually increased up to 138°C.

The mechanical properties of the material obtained w re as follows:

- Density: 0.98 g/cm^3
- Tensile strength: 1.5GPa;
- Shear strength: - 25 MPa;
- Transversal strength: - 25 MPa;
- Ultimate transversal elongation at 25°C: - 70%, and
- Matrix content: 30%.
- Tensile ultra-sonic elastic modulus - 120 GPa

C L A I M S :-

1. Polyolefin composite material based on fiber and a matrix of a polyolefin, selected from polyethylene and polypropylene, possessing improved mechanical properties, comprising a net-work of fibers and matrix which have a molecular weight of above 500,000, said net-work being held together by compressed and crystallized molecular brush layers obtained by swelling of the external surface of said fibers and reciprocal entanglement with it of the polymer matrix.

2. The polyolefin composite material according to Claim 1 possessing a tensile strength of at least 75% of the volume average tenacity of the polyolefin fiber net-work and matrix.

3. The polyolefin composite material according to Claim 1, which have a molecular weight of above 3,000,000.

4. The polyolefin composite material according to Claims 1 or 2, wherein the amount of the matrix is between 3% to 50% by weight of the material.

5. The polyolefin composite material according to Claims 1 to 3, wherein the compressed and crystallized molecular brush layers are obtained by compression and crystallization of the entangled molecular brush layers.

6. The polyolefin composite material according to Claims 1 to 3, wherein the entangled molecular brush layers are obtained by the swelling of the fibers external surface and reciprocal entanglement with it of the polymer in a solution.

7. The polyolefin composite material according to Claim 6, wherein said swelling is obtained by using an organic solv nt.

8. The polyolefin composite material according to Claim 7, wherein said swelling is obtained by using a solution of the matrix forming polymer.

9. The polyolefin composite material according to Claim 7, wherein said organic solvent is selected from the group consisting xylene, decalin, tetralin and paraffin oil or any mixture thereof.

10. A process for the preparation of composite material based on fibers and matrix of ultra-high molecular weight polyethylene, which comprises the steps of:

- swelling said fibers of polyethylene in a solvent or a solution of the matrix forming polymer;
- growing the brush layers from the dissolved polyethylene entangled with said swelled polyethylene fiber surface;
- crystallization of the brush layers, entangled with the fiber surface molecules and with the polymer from the adhered solution;
- compressing the supermolecular structures accumulated on the fiber surface, and
- molding under heating and compression the resulted semi-product coating.

11. The process according to Claim 10 wherein the concentration of the polyethylene in the solvent is between 0.1% to 10% by weight.

12. The process according to Claims 10 and 11, wherein said swelling and growing the brush layers are carried out at a temperature which is above the dissolution point of the polyolefin fibers without loading, being below its dissolution point under the current loading.

13. The process according to Claims 10 to 12, wherein during said swelling and growing the brush layers a tension is applied by a force of between 0.1% to 30% of the force of break of a polyolefin object for a period up to 40 minutes with said solution.

14. The process according to Claims 10 to 13, wherein the temperature during the crystallization is between 20° to 120°C.

15. A polyolefin material consisting of unidirectional fibers, yarns, layers or cloths, substantially as described in the specification and in anyone of Claims 1 to 9.

16. A process for the preparation of a composite material based on a fiber and matrix of ultra-high molecular weight polyethylene, substantially as described in the specification and in any one of Claims 10 to 14.

FIGURE 1

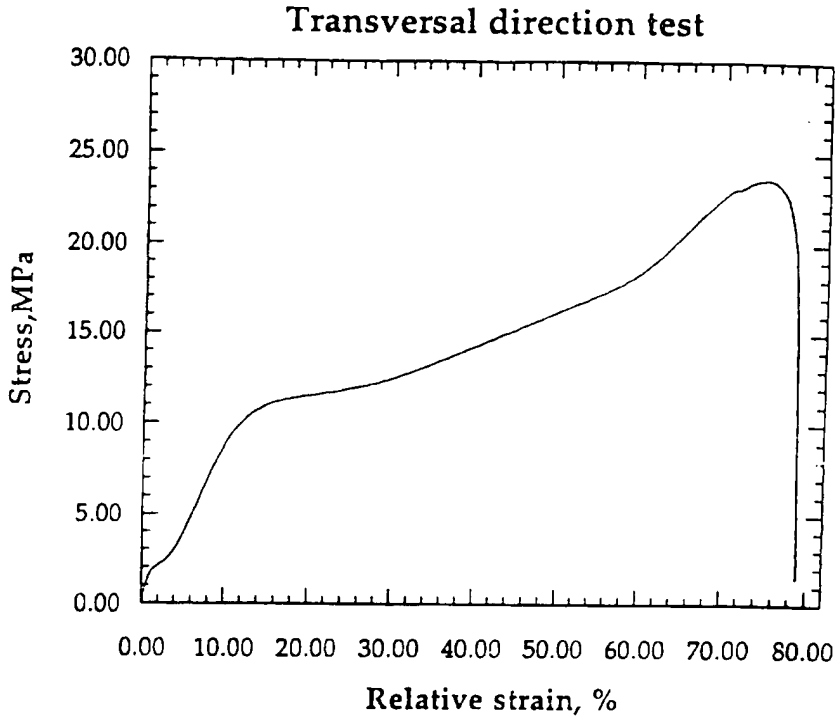
Transversal direction test
30.00
25.00
20.00
15.00
10.00
5.00
0.00
Stress,MPa
0.00
10.00
20.00
30.00
40.00
50.00
60.00
70.00
80.00
Relative strain, %

FIGURE 2

FIGURE 3

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INTERNATIONAL SEARCH REPORT

International application No.
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A. CLASSIFICATION OF SUBJECT MATTER

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According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

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Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

APS & STN
search terms: UHMWPE, composite, matrix, solvent, swelling, fibers

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 5,160,472 A (ZACHARIADES) 03 November 1992, see entire document.	1-4 & 10-11
X	US 4,944,974 A (ZACHARIADES) 31 July 1990, see entire document.	1-4 & 10-11
X	TEISHEV et al., Polyethylene Fibers-Polyethylene Matrix Composites: Preparation and Physical, Journal of Applied Polymer Science, October 1993, pages 503-512.	1-4 & 10-11
A	US 5,198,281 A (MUZZY et al.) 30 March 1993, see entire document.	1

☐ Further documents are listed in the continuation of Box C. ☐ See patent family annex.

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"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art

"&" document member of the same patent family

Date of the actual completion of the international search	Date of mailing of the international search report
05 MARCH 1997	26 MAR 1997

Name and mailing address of the ISA/US	Authorized officer
Commissioner of Patents and Trademarks Box PCT Washington, D.C. 20231	TERREL MORRIS
Facsimile No. (703) 305-3230	Telephone No. (703) 308-2351

INTERNATIONAL SEARCH REPORT

International application No.
PCT/IL96/00095

Box I Observations where certain claims were found unsearchable (Continuation of item 1 of first sheet)

This international report has not been established in respect of certain claims under Article 17(2)(a) for the following reasons:

1. ☐ Claims Nos.:
because they relate to subject matter not required to be searched by this Authority, namely:

2. ☐ Claims Nos.:
because they relate to parts of the international application that do not comply with the prescribed requirements to such an extent that no meaningful international search can be carried out, specifically:

3. ☒ Claims Nos.: 5-9 & 12-16
because they are dependent claims and are not drafted in accordance with the second and third sentences of Rule 6.4(a).

Box II Observations where unity of invention is lacking (Continuation of item 2 of first sheet)

This International Searching Authority found multiple inventions in this international application, as follows:

1. ☐ As all required additional search fees were timely paid by the applicant, this international search report covers all searchable claims.

2. ☐ As all searchable claims could be searched without effort justifying an additional fee, this Authority did not invite payment of any additional fee.

3. ☐ As only some of the required additional search fees were timely paid by the applicant, this international search report covers only those claims for which fees were paid, specifically claims Nos.:

4. ☐ No required additional search fees were timely paid by the applicant. Consequently, this international search report is restricted to the invention first mentioned in the claims; it is covered by claims Nos.:

Remark on Protest

☐ The additional search fees were accompanied by the applicant's protest.

☐ No protest accompanied the payment of additional search fees.